10/532639
JC12 Rec'd PCT/PTC 22 APR 2005

NOVEL FUEL WITH HIGH OCTANE INDEX AND REDUCED LEAD CONTENT

The present invention relates to novel fuel formulations having a high octane number and reduced contents of organo-lead compounds, which may be used for fueling controlled-ignition internal combustion engines, in particular those fitted in aircraft, or engines with a high compression ratio.

It is known that, prior to being made available on the market, fuels intended for fueling controlled-ignition internal combustion engines must satisfy precise physicochemical characteristics to ensure that the user obtains high mechanical performance and, at the same time, to minimize the sources of pollution, whether they are generated by the exhaust gases or by the product itself during its handling or storage. These characteristics, which may vary substantially from one fuel to another, must remain within a range defined by official specifications collated and published by qualified bodies, such as AFNOR in France or ASTM in the United States. Among these specifications, that relating to the octane number, i.e. the number measuring the anti-knock value of a fuel by comparison with a "reference" spirit, is an essential characteristic, since it reflects the combustion performance of the fuel in the engine cylinders, and in particular its resistance to pinking, i.e. its resistance to uncontrolled bulk self-combustion.

Thus, two types of octane number are distinguished in the art for spirits intended for fueling engines fitted in motor vehicles: the RON (Research Octane Number) and the MON (Motor Octane Number), which are referred to, respectively, in the profession as F1 and F2.

In the field of aviation, and more specifically for aircraft fitted with controlled-ignition engines, the fuels available on the market must be produced with care and must in particular have very good resistance to pinking for obvious reasons of reliability and operating safety at altitude, and above all given the severe and particular conditions of use of these engines, which run at full load during the takeoff phase. Two specific octane numbers have consequently been defined and incorporated into the specifications of aircraft spirit, namely:

- the MON or motor octane number (which replaces the old number, previously referred to as F3 in the profession), which is aimed at assessing correct functioning of the motorization as a whole during normal running, i.e. at altitude and at stabilized speed; and
- the supercharge octane number, also known as F4 or performance number, which reflects the combustion performance needs of the engine on takeoff.

Thus, a fuel whose commonly used trade name is "AVGAS 100LL" corresponds to a spirit for controlled-ignition piston aircraft engines, the MON of which should be, according to standard ASTM D910-01 (Standard Specification for Aviation Gasolines) or the equivalent British standard DEF STAN (Defense Standard) 91-90 of 8 May 1996, greater than or equal to 99.5; and the F4 greater than or equal to 130. The abbreviation "LL" means "low lead", i.e. the lead content of the fuel, generally originating from alkylleads, should be, according to this standard that is currently in force, less than or equal to 0.56 gram per liter of spirit.

It is known that the spirits manufactured directly by distillation of crude petroleum do not have the required characteristics, in particular the required octane characteristics, to allow them to be placed directly on the aviation market. The refiner must therefore, during their manufacture, perform mixing of various hydrocarbon bases in order to obtain products which, with the optional addition of additives, will comply with the various specifications required for their marketing. These bases may consist, for example and in a nonlimiting manner, of:

- light distillation fractions essentially containing paraffins containing 4 or 5 carbon atoms;
- hydrocarbons derived from the alkylation of gases containing 1 to 4 carbon atoms, free of aromatic or olefinic molecules;
- light spirits originating from the direct distillation of crude petroleum, whether these spirits are isomerized or nonisomerized; and
- hydrocarbons mainly containing aromatic compounds having, by nature, high octane numbers.

However, the octane requirements of fuels for aircraft engines are so high that it is generally impossible to economically produce such fuels, having the required specifications, without resorting to the massive addition of additives. This is why refiners commonly add an organolead compound in order to ensure the MON and F4 specifications of spirit of type 100LL, in accordance with standard ASTM D910-01. This compound is generally tetraethyllead ($C_8H_{20}Pb$), abbreviated as TEL, the content of which in the fuel should be in accordance with the standard and should not exceed 0.56 gram of lead per liter of spirit.

It is known, however, that the use of lead in fuels, on account of its harmful nature to health, has been terminated in Europe since January 1, 2000 and since January 1, 1996 in the United States, for motor vehicle spirits, but not for fuels intended for controlled-ignition aircraft engines, by special exemption from the Environmental Protection Agency (EPA). Consequently, it is now acknowledged that aircraft spirit remains an important source of pollution for the atmosphere.

The problem of reducing lead content in certain aircraft engine spirits, and especially AVGAS 100LL, or even of eliminating it, is thus acutely relevant and a solution will need to be found in the short or medium term. However, replacement alternatives have already been proposed, for instance the use of:

- a lead-free spirit for aircraft of the type 82UL (specified by ASTM D6227-00) or for motor vehicles, but the anti-pinking characteristics of motor vehicles are insufficient to be able to feed all the existing fleet;
- a lead-free aviation spirit composition, but with additions of oxygenated compounds such as MTBE or ETBE, as described in patent WO 02/22766;
- a spirit that is also lead-free, formulated with, inter alia, known hydrocarbon bases, an alkyl tert-butyl ether, an aromatic amine and optionally a manganese compound, as claimed in patent WO 97/44413;
- an aircraft spirit formulation manufactured from standard bases with addition of toluene and an aromatic amine for F4, in accordance with the description of patent WO 94/25545;
- a lead-free spirit manufactured with addition of methylcyclopentadienyl-manganese-tricarbonyl (abbreviated as MMT) in accordance with the teaching of patents EP 0 540 297, EP 0 609 089 and WO 94/17158, or
- a lead-free composition for aircraft spirit, manufactured with addition of triptane, as described in patent WO 98/22556.

All the spirit compositions that are currently available present refiners with technical difficulties of formulation, while at the same time generating additional costs due to the use of numerous additives, or specific hydrocarbon bases, which is made necessary in order to compensate for the absence of or decrease in lead, i.e. the lack of octane, and consequently to achieve the specified MON and F4 targets. Furthermore, the environmental compatibilities of the various additives used at the present time have not yet been entirely demonstrated; thus, all aromatic amines are classified as toxic substances, in the event of absorption by inhalation or ingestion, and especially for the skin. As regards MMT, it is indexed by the EPA as being an atmospheric pollutant that may be potentially hazardous to man.

To manufacture aircraft spirits of 100LL type economically and with reduced environmental risks, refiners are thus confronted with the following alternative:

- either formulating fuels using bases commonly available in refineries, but in which the organolead compounds have been replaced with additions of various additives, or specific hydrocarbon bases, so as to obtain an MON and an F4 in accordance with the specification in force. These additions consequently give rise to extra cost for the refiner and possible environmental drawbacks;

- or to subject the various hydrocarbon bases included in the composition of fuels to expensive treatments in order to increase their octane number and thus reduce or even dispense with the lead, but these various treatments require, however, complex processes that also generate a large additional cost for the refiner.

The research conducted by the Applicant in the field of fuel manufacture has now enabled it to establish, surprisingly, that the precise and rigorous formulation of aviation spirits, from certain hydrocarbon bases generally available in a petroleum refinery, makes it possible to give them a sufficiently high octane number of the F4 type, at least equal to 130, and an MON at least equal to 99.5, while at the same time substantially reducing the content of organolead compounds, and especially of TEL, without having to resort to octane-providing substitution additives.

The aim of the invention is thus to provide novel fuel formulations for controlled-ignition internal combustion engines, made from a mixture of hydrocarbon bases available in a petroleum refinery, and containing an appreciably reduced amount of organolead compounds compared with the formulations of the prior art, and which give these fuels an octane number and characteristics that comply with the standards in force.

To this end, one subject of the invention is a fuel having a lead content of less than or equal to 0.56 gram per liter of fuel, containing at least one first hydrocarbon base (B1) consisting essentially of isoparaffins containing 4 or 5 carbon atoms, and also at least one second hydrocarbon base (B2) consisting essentially of isoparaffins containing 6 to 9 carbon atoms, and optionally at least one complement (B3) consisting essentially of hydrocarbons of alkylaromatic type containing 6 to 11 carbon atoms, in which:

- the content of the base B2 in the fuel is between 45% and 85% by volume and preferably between 50% and 82% by volume, and in that
- the ratio of the volume percentage amounts B1/B2 is between 0.10 and 0.60 and preferably between 0.15 and 0.45.

To this end, a subject of the invention is also a fuel having a lead content of less than or equal to 0.56 gram per liter of fuel, containing at least one first part of isoparaffins containing 4 or 5 carbon atoms, and also at least one second part of isoparaffins containing 6 to 9 carbon atoms, and optionally at least one complementary part of hydrocarbons of alkylaromatic type containing 6 to 11 carbon atoms, in which:

- the content of isoparaffins containing 6 to 9 carbon atoms in the fuel is between 45% and 85% by volume and preferably between 50% and 82% by volume, and in that

- the ratio of the volume percentage amounts of isoparaffins containing 4 or 5 carbon atoms/isoparaffins containing 6 to 9 carbon atoms is between 0.10 and 0.60 and preferably between 0.15 and 0.45.

In the present description:

- the term "essentially consisting of" means the presence of a large amount, preferably greater than 70% by volume, of cited compounds in the corresponding hydrocarbon base;
- the lead contents are cited by reference to the methods for measuring lead contents, described in standards ASTM D3341 (iodine monochloride method) or ASTM D5059 (X-ray spectrometry method);
- the MON and the F4 are measured, respectively, in accordance with standards ASTM D2700 and ASTM D909.

According to the invention, the ratio of the volume percentage amounts B3/B2 is between 0.00 and 0.60 and preferably between 0.00 and 0.55; alternatively, the ratio of the volume percentage amounts of hydrocarbons of alkylaromatic type containing 6 to 11 carbon atoms/isoparaffins containing 6 to 9 carbon atoms is between 0.00 and 0.60 and preferably between 0.00 and 0.55.

The use of at least the two fractions (B1), (B2), preferentially along with at least the fraction (B3), and their incorporation in the abovementioned relative amounts, allows the refiner to formulate fuels that simultaneously have a high octane number and a reduced lead content, of less than or equal to 0.56 gram per liter, preferably less than or equal to 0.42 gram per liter, even more preferably less than or equal to 0.35 gram per liter, entirely preferably less than or equal to 0.28 gram per liter and ideally equal to 0.14 gram per liter of fuel.

Specifically, the fuels according to the invention may be manufactured using hydrocarbon bases available in a standard refinery, and may achieve high octane numbers, in accordance with the strictest standards such as standard ASTM D910-01, while at the same time having a lead content that may be as low as 0.27 g/l, or even less. Thus, with strictly processed bases, it is possible to formulate aircraft fuels having a lead content of only 0.14 g/l. The refiner thus adds less lead derivative than previously.

In the present description, reference is made mainly to fuels for aircraft engines, but the fuels in accordance with the invention may be used in fields other than aviation, and especially for fueling, alone or as a mixture, controlled-ignition engines for vehicles of all types, especially aircraft. The use of the fuel according to the invention is particularly advantageous for fueling the engines of competition vehicles or the like, i.e. for engines with a high compression ratio, requiring fuels with a very high octane number. The fuel that is the subject of the present invention

may also be used for fueling, alone or as a mixture, systems of very diverse nature, for example a fuel processing unit, such as a reformer, coupled to a fuel cell.

The first hydrocarbon base (B1) used for the manufacture of the fuels in accordance with the invention belongs to the family of paraffinic hydrocarbons and may be, for example, a light base containing at least 80% by volume and preferably at least 90% by volume of isoparaffinic molecules containing 4 or 5 carbon atoms and preferably 5 carbon atoms. Even more preferably, isopentane constitutes at least 90% by volume of the molecules containing 5 carbon atoms.

This light paraffinic base may originate, for example, from a fractionation of the lightest fraction of the distillate produced by the atmospheric distillation of crude petroleum or from an alkane isomerization unit.

Advantageously, this hydrocarbon fraction may contain up to 10% by volume of isoparaffins containing 4 carbon atoms; isobutane constitutes at least 5% by volume of said isoparaffins, when there is a need to increase the vaporization of the fuel to feed the controlled-ignition engine.

The second base used (B2) typically contains at least 80% by volume and preferably at least 90% by volume of isoparaffins containing between 6 and 9 carbon atoms and preferably 8 carbon atoms. Isooctanes constitute at least 70% by volume and preferably at least 75% by volume of these isoparaffinic hydrocarbons containing 8 carbon atoms.

Such a hydrocarbon base may originate from various processes for processing crude petroleum, generally present in a petroleum refinery. In particular, this isooctane-rich hydrocarbon fraction, also known in the profession as "alkylate", may be produced, for example, via the process for the alkylation of isobutane with light olefins.

An alternative consists in replacing some of this isoparaffinic fraction and simultaneously reducing the proportion of alkylate, which is a petroleum base whose manufacturing cost is relatively high, with a hydrocarbon fraction originating from a unit for isomerizing light spirits, these spirits being derived from the distillation of crude petroleum.

The complement used (B3) is a hydrocarbon fraction containing 6 to 11 carbon atoms, of which the content of aromatic compounds containing 6 to 9 carbon atoms is typically greater than or equal to 80% by volume and preferably greater than or equal to 85% by volume. Even more preferably, these aromatic compounds contain 7 carbon atoms and are toluene, the content of which in the complement (B3) is greater than or equal to 45% by volume and preferably greater than or equal to 50% by volume. This hydrocarbon base used in the formulation of the spirits for aircraft engines generally originates from a manufacturing process known as spirit

"reforming", available in particular in a petroleum refinery. This process makes it possible, by means of a set of chemical reactions taking place at high temperature and high pressure, necessarily in the presence of a suitable catalyst, to convert straight-chain or cyclic molecules contained in the heaviest spirits, for example those produced by the direct distillation of crude petroleum, into more stable branched and cyclic aromatic hydrocarbons. These aromatic hydrocarbons are generally referred to as "reformates" in the profession and have a high octane number.

In addition to the bases (B1), (B2) and (B3), the fuel according to the invention may contain many other bases. These may be chosen especially from all the bases liable to be included in the composition of the spirits. These bases may be derived from standard refining operations (for example, but in a nonlimiting manner, the distillation of crude petroleum, catalytic cracking, hydrocracking, reforming, isomerizing, alkylating, etc. processes), but may also comprise synthetic hydrocarbons such as those obtained by oligomerization of olefins or by Fischer-Tropsch synthesis.

Preferably, these additional bases are chosen from those having a distillation range of between 25°C and 175°C (determined according to standard ASTM D 86) and even more preferably between 75°C and 135°C. A person skilled in the art will readily know how to determine the nature and amounts of the additional bases liable to be incorporated into the fuel according to the invention, given the application for which this fuel is intended and the bases available in the refinery.

Each base included in the composition of the fuel according to the invention, i.e. (B1), (B2), (B3) and also any additional base, may advantageously have been totally or partially subjected to a desulfurization and/or deazotization treatment and, optionally, a dearomatization treatment, at any stage in its production. For example, it is possible to use bases that have been hydroprocessed under more or less severe conditions (comprising hydrodesulfurization and/or saturation of the aromatic and olefinic compounds and/or hydrodeazotization).

The fuel according to the invention advantageously has a sulfur content (determined according to standards ASTM D1266 or ASTM D2622) of less than or equal to 500 ppm by weight, preferably less than or equal to 100 ppm by weight, even more preferably a sulfur content of less than or equal to 50 ppm by weight or even 10 ppm by weight.

The fuel according to the invention may contain one or more additives that a person skilled in the art can readily select from the numerous additives conventionally used for fuels. The choice of these additives depends essentially on the application for which the fuel is intended. Mention is especially made, but in a nonlimiting manner, of corrosion-inhibiting, antifreeze or antistatic additives,

additives for improving the cold properties, tracer additives or detergent additives, and mixtures thereof.

For example, when the fuel is intended for aviation use, it may contain, inter alia, at least one antioxidant chosen from sterically hindered phenols (for instance 2,6-di-t-butyl-4-methylphenol (BHT), 2,6-di-t-butylphenol and 2,4-dimethyl-6-t-butylphenol).

The determination of the contents of other possible hydrocarbons and common additives in the fuel, in order to make it comply with the regulations in force in the art or with particular characteristics, is within the competence of a person skilled in the art and poses no particular technical problem.

The invention also relates to a process for preparing fuel with a low lead content and a high octane number, in which at least one first hydrocarbon base (B1) consisting essentially of isoparaffins containing 4 or 5 carbon atoms, and at least one second hydrocarbon base (B2) consisting essentially of isoparaffins containing 6 to 9 carbon atoms, and, preferably, at least one supplement (B3) consisting essentially of hydrocarbons of alkylaromatic type containing 6 to 11 carbon atoms, and, optionally, additives that are common for this type of fuel, are mixed together, by means known in the art, in amounts such that:

- the content of the base B2 in the fuel is between 45% and 85% by volume and preferably between 50% and 82% by volume, and in that
- the ratio of the volume percentage amounts B1/B2 is between 0.10 and 0.60 and preferably between 0.15 and 0.45.

Finally, the invention relates to the use of such a fuel for reducing the polluting emissions of a controlled-ignition engine. Specifically, besides reducing the pollution due to the reduction in the lead content in the fuel, this reduction also results in a decrease in the content of methyl bromide, produced during the combustion of AVGAS 100LL. This methyl bromide, which has known destructive effects on the atmospheric ozone layer, originates from the dibromoethane that is added (referred to as a “scavenger” in the profession) during the manufacture of 100LL spirit so as to trap the lead in the engine cylinders, and allow its removal by volatility after the combustion cycle.

According to one embodiment, the lead content is less than 0.56 gram per liter of fuel.

According to one embodiment, the content of the base B2 is between 55% and 75% by volume.

According to one embodiment, the content of the base B1 is between 12% and 30% by volume.

According to one embodiment, the fuel comprises less than 5% by volume of cycloparaffins containing from 5 to 8 carbon atoms.

According to one embodiment, the ratio of the volume percentage amounts B3/B2 is between 0.1 and 0.60 and preferably between 0.2 and 0.45.

According to one embodiment, the lead content is less than or equal to 0.26 and preferably less than 0.14 gram per liter of fuel.

According to another embodiment, the lead content is between 0.10 and 0.28 and preferably between 0.14 and 0.26 gram per liter of fuel.

According to one embodiment, the Net Heat of Combustion (determined according to standard ASTM D4529) is between 39.1 MJ/kg and 43.5 MJ/kg, preferably between 39.1 MJ/kg and 43 MJ/kg, advantageously between 39.1 MJ/kg and 42.2 MJ/kg and more advantageously between 39.1 MJ/kg and 41.3 MJ/kg.

The reduction of the lead content in the fuel, in accordance with the invention, is particularly advantageous for the following reasons, alone or in combination:

- it complies with the existing specifications and does not have the environmental drawbacks of the usual fuels, intended for the same applications, for a manufacturing cost that is substantially lower than said usual fuels;
- it does not incorporate any octane-providing additives other than a reduced amount of organolead compounds;
- its environmental qualities are more suited to the current requirements;
- its lower lead content allows the scavenger content to be reduced; and
- it is compatible with all the other fuels for controlled-ignition engines.

Other characteristics and advantages of the invention will become apparent in the detailed examples that follow, which have no limiting nature.

EXAMPLES

Example 1

The Applicant formulated 4 fuels (listed C1 to C4) in accordance with the invention using the hydrocarbon bases B1, B2 and B3 generally found in a petroleum refinery, and the compositions of which are indicated in table 1 below, and 4 other mixtures not within the scope of the invention (listed C5 to C8).

Table 1
Composition of the 3 bases B1, B2 and B3

B1	C5 isoparaffins C5 and C4 paraffins C4 and C5 olefins	95.47% mass 3.34% mass 1.19% mass
B2	C8 isoparaffins C6, C7 and C9 isoparaffins C5, C10 and C11 isoparaffins C4 and C11 paraffins C9 olefins C11 aromatics	82.87% mass 10.02% mass 5.75% mass 1.29% mass 0.02% mass 0.05% mass
B3	C7 aromatics C8 aromatics C9 aromatics C6, C10 and C11 aromatics C4 to C11 paraffins C4 to C9 isoparaffins Others	51.72% mass 26.36% mass 9.84% mass 1.74% mass 2.54% mass 5.99% mass 1.81% mass

For each fuel thus manufactured, the main physicochemical characteristics (cf table 2) were measured in accordance with standard ASTM D910-01.

Table 2
Main characteristics of the aviation spirit 100LL and corresponding analysis methods

	Specifications ASTM D-910-01
F4 ASTM D909	min 130.0
MON ASTM D2700	min 99.5
NHC MJ/kg ASTM D4529	min 43.5
VP (38°C, KPa) ASTM D5191	min 38.0 max 49.0
10% evaporated °C ASTM D86	max 75
50% evaporated °C ASTM D86	max 105
90% evaporated °C ASTM D86	max 135
Final point ASTM D86	max 170
Pb g/l ASTM D2392	max 0.56

NHC: Net heat of combustion
VP: Vapor Pressure

The results of the measurements are given in table 3

Table 3
Manufacture of the fuels and characteristics thereof according to ASTM D910-01

Mixtures	C1	C2	C3	C4	C5	C6	C7	C8	Specifications ASTM D-910-01
B1 (% v)	21.2	21.1	12.0	17.3	37.5	7.0	61.5	19.8	--
B2 (% v)	50.8	57.9	68.7	57.5	40.0	91.2	20.8	31.2	--
B3 (% v)	28.0	21.0	19.3	25.2	22.5	1.8	17.7	49.0	--
B1/B2	0.42	0.36	0.17	0.30	0.94	0.07	2.96	0.63	
B3/B2	0.55	0.36	0.28	0.44	0.56	0.02	0.85	1.57	
F4 ASTM D909	150.0	130.0	131.8	130.0	130.9	130.8	**105.7**	132.3	min 130.0
MON ASTM D2700	105.6	102.0	102.0	101.4	102.8	103.2	100.8	99.8	min 99.5
NHC MJ/kg ASTM D4529	43.5	43.8	43.8	43.6	43.7	44.5	44.0	**42.6**	min 43.5
VP (38°C, KPa) ASTM D5191	48.0	49.0	38.0	43.6	**69.3**	**34.5**	**100.0**	42.9	min 38.0 max 49.0
10% evapo-rated °C ASTM D86	62.2	61.6	72.0	66.4	42.8	**76.1**	14.6	65.9	max 75
50% evapo-rated °C ASTM D86	103.7	101.9	105.0	104.5	95.9	102.3	85.23	**109.8**	max 105
90% evapo-rated °C ASTM D86	122.7	118.9	118.2	121.3	119.2	108.8	115.9	134.2	max 135
Final point °C ASTM D86	157.2	152.8	151.9	155.6	153.4	140.9	149.9	**170.6**	max 170
Pb g/l ASTM D2392	0.54	0.30	0.28	0.27	0.38	0.30	0.27	0.23	max 0.56

It is seen in table 3 that the fuels formulated in accordance with the present invention (C1 to C4) satisfy the main characteristics of ASTM D910-01 for

AVGAS 100LL. In contrast, when the content of B2 in the fuels (C5 to C8) is not between 45% and 85% by volume, or when the ratio B1/B2 is not within the range 0.10-0.60, the specifications are not met. This table also teaches that it is possible to formulate a fuel with a lead content equal to 0.27 gram per liter of fuel while at the same time satisfying the standard in force (C4).

Example 2

This example is identical to example 1, but the fuels C9 to C16 were formulated using purified bases B1, B2 and B3, the respective new compositions of which are indicated in table 4 below.

Table 4

Composition of the 3 bases

B1	C5 isoparaffins	100.00% mass
B2	C8 isoparaffins C7 isoparaffins	99.97% mass 0.03% mass
B3	C7 aromatics C5 and C8 aromatics	99.95% mass 0.05% mass

The results of the measurements are given in table 5

Table 5

Manufacture of the fuels and characteristics thereof according to ASTM D910-01

Mixttures	C9	C10	C11	C12	C13	C14	C15	C16	Specifi-cations ASTM D-91001
B1 (% v)	26.1	16.2	17.2	19.3	29.5	38.5	7.5	20.8	--
B2 (% v)	47.9	83.6	68.1	54.8	28.8	43.2	89.2	30.7	--
B3 (% v)	26.0	0.2	14.7	25.9	41.7	25.3	3.3	48.5	--
B1/B2	0.54	0.19	0.25	0.35	1.02	0.89	0.08	0.68	
B3/B2	0.54	0.01	0.21	0.47	1.44	0.58	0.03	1.58	
F4 ASTM D909	155.0	134.9	130.1	130.0	130.4	132.2	130.5	142.0	min 130.0
MON ASTM D2700	107.9	105.4	102.7	101.2	99.6	104.4	103.3	99.7	min 99.5
NHC MJ/kg ASTM D4529	43.5	44.7	44.0	43.5	**42.8**	46.7	44.6	**42.4**	min 43.5
VP (38°C, KPa) ASTM D5191	48.9	38.0	38.0	39.6	**52.1**	**67.0**	**25.6**	39.6	min 38.0 max 49.0
10% eva-porated °C ASTM D86	61.6	73.6	73.1	70.8	57.8	51.4	**85.7**	70.1	max 75
50% eva-porated °C ASTM D86	98.6	95.4	98.5	100.4	101.2	101.9	98.6	**105.2**	max 105

90% evaporated °C ASTM D86	102.1	95.6	99.1	101.8	106.0	109.1	96.0	107.3	max 135
Final point °C ASTM D86	111.9	103.3	108.2	111.9	117.1	118.7	104.5	119.5	max 170
Pb g/l ASTM D2392	0.54	0.28	0.18	0.14	0.14	0.23	0.17	0.14	max 0.56

As in example 1, the fuels formulated in accordance with the present invention (C9 to C12) satisfy the main characteristics of ASTM D910-01 for AVGAS 100LL. Furthermore, with the use of purified bases, the content of 0.14 gram of lead per liter of fuel may be achieved (C12), while at the same time satisfying the specifications for the spirit 100LL. In contrast, when the content of the base B2 in the fuels (C13 to C16) is not between 45% and 85% by volume, and when the ratio B1/B2 is not within the range 0.10-0.60, the specifications are not met.

Example 3

Given that the "CRC-unleaded Aviation Gasoline Development Group" envisaged in its preliminary report of 18 November 1999 a possible relaxation of the specification of the Net Heat of Combustion for the spirit 100LL, which may be up to several percent of the nominal value, the Applicant has established the ranges of formulations for fuels satisfying the specifications of ASTM D910-01, for various contents of lead, and several values of the minimum NHC, ranging from 43.5 to 39.1 MJ/kg, when these fuels are manufactured with industrial bases of petroleum refinery type, or purified products. The results are presented in tables 6 and 7.

1/Industrial bases

The bases B1, B2 and B3 have the physicochemical characteristics in accordance with table 1 above.

Table 6

Ranges of formulations for the spirit 100LL starting with industrial bases, for various lead contents and several values of the minimum NHC

INDUSTRIAL BASES						
NHC (ASTM D4529) % relaxation	>=43.5 0	>=43.0 -1%	>=42.8 -2%	>=42.2 -3%	>=41.3 -5%	>=39.1 -10%
Pb content (g/l of fuel)						
0.00	D0	D0	D0	D0	D0	D0
0.08	D0	D0	D0	D0	D0	D0
0.09	D0	D0	D0	D0	D0	D0
0.10	D0	D0	D0	D0	D0	D0
0.11	D0	D0	D0	D0	D0	D0
0.12	D0	D0	D0	D0	D0	D0
0.13	D0	D0	D0	D0	D0	D0
0.14	D0	D0	D0	D0	D0	D0
0.15	D0	D0	D0	D0	D0	D0
0.16	D0	D0	D0	D0	D0	D0
0.17	D0	D0	D0	D0	D0	D0
0.18	D0	D0	D0	D0	D0	D0
0.24	D0	D0	D0	D0	D0	D0
0.25	D0	D0	D0	D0	D0	D0
0.26	D0	D0	D0	D0	D0	D0
0.27	D1	D4	D7	D9	D12	D13
0.28	D2	D5	D8	D10		D14
0.56	D3	D6		D11		D15

D0 means that there is no possible range of formulation of a spirit 100LL that satisfies the main characteristics of standard ASTM D910-01.

It is seen in table 6 that with hydrocarbon bases or fractions of petroleum origin, generally available in a petroleum refinery, as defined in table 1, the smallest admissible lead content to manufacture a fuel that satisfies the standard in force is 0.27 g/l (D1), irrespective of the adopted value of the minimum NHC of between 43.5 and 39.1 MJ/kg (D4, D7, D9, D12 and D13).

2/Purified bases

The physicochemical characteristics of the bases B1, B2 and B3 are given in table 4 above.

Table 7/Ranges of formulations for the spirit 100LL starting with purified bases, for various lead contents and several values of the minimum NHC

PURIFIED BASES						
NHC (ASTM D4529) % relaxation	>=43.5 0	>=43.0 -1%	>=42.8 -2%	>=42.2 -3%	>=41.3 -5%	>=39.1 -10%
Pb content (g/l of fuel)						
0.00	D0	D0	D0	D0	D0	D0
0.08	D0	D0	D0	D0	D0	D0
0.09	D0	D0	D19	D26	D38	D39
0.10	D0	D8	D20	D27		D40
0.11	D0	D9	D21	D28		D41
0.12	D0	D10	D22	D29		D42
0.13	D0	D11	D23	D30		D43
0.14	D1	D12	D24	D31		D44
0.15	D2	D13	D25	D32		D45
0.16	D3	D14		D33		D46
0.17	D4	D15		D34		D47
0.18	D5	D16		D35		D48
0.28	D6	D17		D36		D49
0.56	D7	D18		D37		D50

D0 means that there is no possibility of formulating a spirit 100LL that satisfies the main characteristics of standard ASTM D910-01.

It is seen in table 7 that, with purified products, as defined in table 4 above, it is possible to formulate an aviation spirit containing 0.14 g/l of lead (D1), while at the same time satisfying the characteristics defined in the standard in force for aviation spirit 100LL. Furthermore, this minimum lead content reaches 0.10 g/l (D8) when the value of the minimum NHC is reduced to 43.0 MJ/kg (1% relaxation), it is 0.09 g/l (D19) for a minimum NHC value of 42.6 MJ/kg (2% relaxation) and less, down to 39.1 MJ/kg (10% relaxation). The fact of characterizing the minimum NHC 1% below the value of the current standard makes it possible to reduce the lead content by about 28%, and this reduction is 36% when the minimum NHC is relaxed by 2% and more.

The fuels thus manufactured in accordance with the invention have various advantages, alone or in combination:

- they have a high octane number, thus corresponding to the F4 and MON octane number specification for aviation spirit 100LL, without the need to add additional octane-providing additives;

- they are environmentally friendly, since they contain a smaller amount of organolead and scavenger compounds;
- they are less expensive to manufacture;
- they make it possible to reduce the pollution impact of lead on the health of living beings;
- finally, they are compatible with the other equivalent hydrocarbons.